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<b>(21) International Application Number:</b> PCT/GB93/01413 <b>(22) International Filing Date:</b> 6 July 1993 (06.07.93)  <b>(30) Priority data:</b> 9214304.9                      6 July 1992 (06.07.92)                      GB  <b>(71) Applicant (for all designated States except US):</b> DU PONT (U.K.) LIMITED [GB/GB]; Coal Road, Leeds LS14 2AL (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> GATES, Allen, Peter [GB/GB]; 13 Fountains Way, Knaresborough HG5 8HU (GB). FELDER, Thomas, Clark [US/GB]; Rosemere, Walton Avenue, Pannal HG3 1EX (GB).  <b>(74) Agent:</b> OVERBURY, Richard, Douglas; Haseltine Lake & Co., Hazlitt House, 28 Southampton Buildings, Chancery Lane, London WC2A 1AT (GB).		<b>(81) Designated States:</b> CA, GB, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> IMAGE FORMATION  <b>(57) Abstract</b>  A driographic printing plate precursor comprises a base substrate, an infrared radiation ablatable ink repellant coating on the substrate, and a transparent cover sheet on the coating. An image is formed on the plate by sequentially exposing areas of the coating to a laser beam to ablate the coating in those areas. The cover sheet and ablation products are then removed.		

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Image Formation

This invention relates to the formation of images directly from electronically composed digital sources and is concerned with the formation of images in this way in dry planography in which there is used a planographic printing plate having background or non-image surface areas which, although not moistened by water or other liquid, will not accept ink.

For many years it has been a long term aim in the printing industry to form images directly from an electronically composed digital database, i.e. by a so-called "computer-to-plate" system. The advantages of such a system over the traditional methods of making printing plates are:

- (i) the elimination of costly intermediate silver film and processing chemicals,
- (ii) a saving of time, and
- (iii) the ability to automate the system with consequent reduction in labour costs.

The introduction of laser technology provided the first opportunity to form an image directly on a printing plate precursor by scanning a laser beam across the surface of the precursor and modulating the beam so as to effectively turn it on and off. In this way, radiation sensitive plates comprising a high sensitivity polymer coating have been exposed to laser beams produced by water cooled UV argon-ion lasers and electrophotographic plates having sensitivities stretching into the visible spectral region have been successfully exposed using low-powered air-cooled argon-ion, helium-neon and semiconductor laser devices.

Imaging systems are also available which involve a sandwich structure which, on exposure to a heat generating infra-red laser beam, undergoes selective (imagewise) delamination and subsequent transfer of materials. Such so-called peel-apart systems are

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generally used as replacements for silver halide films.

It is also known to overcome difficulties inherent with conventional lithography - the best known form of planography - via the use of planographic printing plates which do not require a dampening of the printing plate with an aqueous fountain solution to effectively wet the non-image areas. Such so-called "driographic" plates are typically derived from radiation sensitive plates comprising a substrate coated with a photosensitive layer, said layer being overlaid with a coating of a low surface energy material, which is repellant to printing ink. Alternatively, the ink-repellant layer may be applied directly to the substrate, with the photosensitive layer being coated over the ink-repellant layer. As a further alternative, a single photosensitive, ink-repellant layer containing, for example, a photosensitive silicone polymer, may be coated on a suitable substrate. Several such driographic systems are described, for example, in British Patent Nos. 1,522,228 and 2,034,911 and US Patent Nos. 3,511,178, 3,677,178, 3,894,873, 4,225,663 and 4,724,195.

Radiation sensitive plates for driography as described in the prior art are imaged, in general, by selective removal of areas of the ink-repellant coating to reveal an oleophilic surface which readily accepts printing ink. This may be accomplished in the case of two layer systems, for example, by photochemically changing the adhesion of the ink-repellant layer by exposing the plate to ultraviolet radiation through a photographic positive or negative transparency; the photosensitive layer may be either positive-working, in which case the adhesion of the ink-repellant layer will be strengthened, or negative-working, in which case adhesion will be weakened. In either case, the most weakly adhered coating may subsequently be removed by

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development with a processing solution. Alternatively, plates having a single photosensitive, ink-repellant layer may be imagewise exposed to harden the image areas and then be developed with a processing solution to remove unhardened coating.

Such plates may be used to produce high quality images, but the required imagewise exposure via a photographic transparency detracts from the efficiency of the process. Similar disadvantages are associated with the attendant development step using a processing solution.

A digital imaging technique has been described in US Patent No. 4,911,075 whereby a driographic plate is produced by means of a spark discharge. In this case, a plate precursor comprising an ink-repellant coating containing electrically conductive particles coated on a conductive substrate is used and the coating is ablatively removed from the substrate. Unfortunately, however, the ablative spark discharge provides images having relatively poor resolution.

It is known to improve this feature by the use of lasers to obtain high resolution ablation as described, for example, by P.E. Dyer in "Laser Ablation of Polymers" (Chapter 14 of "Photochemical Processing of Electronic Materials", Academic Press, 1992. p 359-385). Until recently, imaging via this method generally involved the use of high power carbon dioxide or excimer lasers. Unfortunately, such lasers are not well-suited to printing applications because of their high power consumption and excessive cost, and the requirement for high pressure gas-handling systems. Recent developments have, however, led to the availability of more suitable infra-red diode lasers, which are compact, highly efficient and very economical solid state devices. High power versions of such lasers which are capable of delivering up to 3000

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mJ/cm<sup>2</sup> are now commercially available.

Coatings which may be imaged by means of ablation with infra-red radiation have previously been proposed. Thus, for example, a proofing film in which an image is formed by imagewise ablation of a coloured layer on to a receiver sheet is described in PCT Application No. 90/12342. This system is, however, disadvantageous in requiring a physical transfer of material in the imaging step, and such methods tend to give rise to inferior image resolution.

It is an object of the present invention to provide a driographic printing plate precursor which does not require any wet processing and which can be imaged digitally by means of an infra-red diode layer or a YAG laser to provide an image having high resolution.

It is a further object of the present invention to provide a driographic printing plate precursor on which the image is formed directly through the elimination of unwanted material, rather than by means of transfer from another substrate, and which may be imaged directly on a printing press.

According to one aspect of the present invention, there is provided a driographic plate precursor comprising a base substrate carrying an infra-red radiation ablatable ink repellant coating, the coating being covered with a transparent cover sheet.

According to another aspect of the present invention there is provided a method of image formation which comprises

(a) providing a driographic plate precursor comprising:

a base substrate carrying an infra-red radiation ablatable ink repellant coating covered with a transparent cover sheet,

(b) image-wise exposing the precursor by

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directing the beam from an infra-red laser at sequential areas of the coating so that the coating ablates and loses its ink repellancy in those areas to form an image,

- 5 (c) removing the cover sheet and ablation products, and  
(d) inking the image.

The infra-red radiation ablatable ink repellant coating may be in the form of a single layer including  
10 an infra-red radiation ablatable moiety and an ink repellant moiety. Generally, however, the coating is in the form of at least two layers, viz one or more layers providing the coating with its ablatable properties and a further outer layer providing the  
15 coating with its ink repellant properties.

The ablatable properties may be provided by a layer including an ablatable polymer which also absorbs infra-red radiation. Alternatively, an ablatable polymer which does not significantly absorb infra-red  
20 radiation can be used in combination with a material which absorbs infra-red radiation. In this case, the infra-red radiation absorbing material may be present in the same layer as the ablatable polymer or in another layer adjacent thereto. Typically, up to 60%  
25 of infra-red absorbing material may be present and typical coating weights for the ablatable layer(s) are from 0.1 to 5.0 g/m<sup>2</sup>. At least one of the base substrate and the ablatable layer or layers should have ink-receptive properties so that the image produced an  
30 exposure is ink-receptive. Thus, the coating may be a simple mixture of an ink repellant component and an infra-red radiation ablatable component or an interpenetrating polymeric network formed in situ on the substrate. Another alternative comprises a random  
35 block on graft copolymer of an ink repellant monomer units and ablatable monomer units containing infra-red

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absorbing material.

The plate precursor may contain one or more additional layers so as to increase adhesion of the coating to the substrate or to increase adhesion between layers, improve resistance to abrasion, or enhance the performance of the system in other respects.

The base substrate employed in the present invention can be any substrate suitable for the preparation of printing plates. Examples of such substrates are paper, plastics materials, metals, or plastics materials or paper coated with metal by lamination or by any other suitable method. It is advantageous to employ substrates with good rigidity to preserve dimensional stability. Preferred substrates are metals, or plastics, or metallised plastics where there is a need for high reflectivity for infra-red radiation so as to 'trap' the radiation in the overlying coating.

Suitable polymers for the ablatable layer(s) are those which thermally decompose to products which are volatile at ambient temperature. A wide variety of polymers has been found to function acceptably. Suitable examples include self-oxidising binders such as nitrocellulose and modified nitrocellulose as described in, for example, Cellulose and its Derivatives, by Ister and Flegien; non-self-oxidising binders, for example ethylcellulose, (meth)acrylic polymers and copolymers, such as poly(methyl methacrylate), poly(hydroxyethyl methacrylate), poly(n-butyl acrylate), poly(lauryl acrylate-co-methacrylic acid), etc., many of which are available commercially as Elvacite® resins from Du Pont or Neocryl® resins from ICI; styrenic resins such as polystyrene and poly(alpha methyl)styrene; rubbers based on isoprene; poly(vinylbutyrates) and poly(hydroxy butyric acid);

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- beta lactones; polylactic acid, and its copolymers with glycolic acid and valeric acid, and other polyesters; vinyl chloride-vinyl acetate copolymers; polyurethane; polycarbonates and carbonate copolymers; polysulphones and sulphone copolymers. In general acrylic polymers and self-oxidising polymers are most preferred. Also preferred are resins which decompose according to so-called "chemical amplification" schemes described by Frechet et al (J. Imaging. Sci., 30(2), (1986), 59-64);
- 10 Ito and Willson ("Polymers in Electronics", ACS Symposium Series, 242, T. Davidson, Ed., ACS, Washington, DC, (1984) p. 11); E. Reichmanis and L.F. Thompson (Microelectronic Engineering, 13, (1991), 3-10); and others. In these systems, acid-catalysed
- 15 degradation of specific ester, ether, or carbonate moieties leads to generation of carbon dioxide and other gases, and regeneration of the catalyst acid, providing amplification. Specific polymers conforming to chemical catalysis structural criteria are
- 20 poly(propylene carbonate) (supplied as QPAC® by Air Products, Allentown, Pa.), poly(4-t-butoxycarbonyloxystyrene sulphone), poly(p-tert-butoxycarbonyloxy-alpha-methylstyrene), and various polyurethanes which are described in PCT Application
- 25 No. 90/12342. Systems have also been described by Y. Jiang and J.M.J. Frechet (Macromolecules, 24 (12), 1991, 3528-32) and C.G. Wilson et al (Proc. IUPAC, Macromol, Symp., 28th, 1982, 448) in which a polymer with a ceiling temperature lower than the ambient is
- 30 end-capped, conferring ambient stability. Removing the protecting group or otherwise initiating degradation drops the ceiling temperature and the polymer spontaneously decomposes. Specific examples of such polymers are acetyl-capped poly(phthalaldehyde) and
- 35 poly(vinyl-tert-butyl carbonate sulphone).

In the case where it is necessary to include a

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material capable of sensitising the ablatable polymer to infra-red radiation, this may be any suitable substance which absorbs infra-red radiation such as an infra-red absorbing sensitizing dye or, preferably, carbon black. Commercial predispersions of carbon black in suitable binders are especially preferred. Suitable commercial materials are, for example, Dispercel® CBJ-A (Pigment Black 7 in nitrocellulose) and Magnacryl (Pigment Black 7 in acrylic resin), both available from Tennant-KVK Ltd, London, England; Microlith® CWA (Pigment Black 7 in acrylic resin), Microlith® CK (Pigment Black 7 in vinyl chloride-vinyl acetate), and Microlith® CA (Pigment Black 7 in ethyl cellulose), available from Ciba-Geigy Pigments (Manchester, England). Suitable sensitising dyes are cyanines, or variations of cyanines in which the central conjugation system contains squarylium, croconium, cyclopentenyl, or other structures capable of inducing appropriate bathochromic shifts, as described in, for example, Infrared Sensitizing Dyes, M. Matsuoka, Ed., Plenum Press, New York, NY (1990). Infra-red sensitising dyes are available from Sumitomo Chemical (Japan), Eastman Chemicals (Rochester, New York, USA), and other suppliers. For sensitisation to 830 nm diode output, certain squarane dyes are preferred as described in US Patent No. 5,019,549. For YAG laser exposure at 1064 nm, Cyasorb IR 165 from American Cyanamid is preferred. Infra-red sensitising dyes can also be mixed with carbon black.

Optional additives to the ablatable layer include materials which thermally degrade to gaseous products (blowing agents), for example, azodicarbonamide, sulphonyl hydrazide, and dinitrosopentamethylene tetramine (Porofor® products available from Bayer, UK).

When an acid-catalysed degradable polymer is used in the ablatable layer, materials which thermally degrade

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to produce acid can be added to the layer. Such materials include iodonium, sulphonium, and phosphonium salts, organic esters such as 2,6-dinitrobenzyl tosylate, oxime sulphonates, dicarboximide sulphonates, and triazines. These materials are available from Ciba-Geigy (Manchester, England), Akzo (Longjumeau, France), and Eastman Kodak (Rochester, New York, USA). Additives which improve coating quality may be incorporated, and these include fluorinated surfactants (such as Zonyl® surfactants from Du Pont and Fluorad® surfactants from 3M), silicone-based materials (Sil-Wet® products from Dow-Corning), and other well-known classes of surfactants. Additives which improve adhesion to either the substrate or the overlying ink-repellant layer may be incorporated. Such materials include chlorosilane or methoxysilane bonding agents from Dow-Corning (Reading, England).

The ink-repellant properties of the coating are provided by a suitable ink-repellant material providing the required degree of toughness, impermeability to gases, adhesion to its underlayer and ink repellency. Such materials include fluropolymers and silicone polymers, for example poly(dimethylsiloxane). The preferred materials for producing ink-repellant coatings with the required characteristics are silicone oligomers which cure by an addition mechanism. Suitable silicone oligomers for this purpose are available, for example, from Dow Corning SA (Seneffe, Belgium) under the trade name Syl-Off®, and from Thomas Goldschmidt AG (Essen, Germany) under the trade name TEGO® RC. For example Dow-Corning Syl-Off® 7046 (30% reactive siloxane polymer, thought to be vinylsiloxane) may be combined with Dow-Corning Syl-Off® 7048 (>95% polymethylhydrogensiloxane, thought to contain a platinum catalyst) to produce a coatable mixture which can be heat cured to produce an ink-repellant film.

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- Additives are available from Dow-Corning which will improve the adhesion and toughness of the silicone film, such as Syl-Off® 297 (anchorage additive, a mixture of acetoxysilane and epoxy functional silane),
- 5 and Syl-Off® 7210 (controlled release additive, 60% silicone resin solution in xylene). Fluoropolymer oligomers are available, from example, from Du Pont (Wilmington, Delaware, USA) under the trade name Zonyl®.
- 10 In the case where the ink repellent material is present as a separate layer overcoated onto an ablatable layer, the coating weight of ink repellent material may be from 0.1 to 5.0 g/m<sup>2</sup> and the ablatable material and the ink-repellent material may be
- 15 successively coated on the substrate by means of coating techniques such as spin coating, bar coating, dip coating, reverse roll coating, gravure coating, knife coating and vacuum or plasma deposition processes. The layers may be cured by baking at 50-
- 20 180°C for between 30 seconds and 10 minutes, or by exposure to ultra-violet radiation in the case where the layers are photocrosslinkable.
- In the alternative case wherein the ablatable material and the ink-repellent material are combined in
- 25 a single layer, said single layer comprises (i) either (a) a suitable ablatable ink-repellent material, such as a fluoropolymer or silicone polymer, for example a polysiloxane, or (b) a combination of an ablatable material and an ink-repellent material and, where
- 30 necessary, (ii) a material capable of sensitising said ablatable material to infra-red radiation. Such sensitising material may be any suitable substance which absorbs infra-red radiation, such as an infra-red absorbing sensitising dye or, preferably, carbon black.
- 35 The single layer may also contain a sensitivity enhancing agent such as a blowing agent or a non-

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absorbing, thermally degradable acid-release compound, in addition to additives which improve coating quality and adhesion. The layer may be coated on the substrate by means of the coating techniques previously

5 described, and cured.

The driographic plate precursor includes a transparent cover sheet overlaid on the surface of the coating. Thus, in the case where the ink repellent material and the ablatable material are in separate  
10 layers, the sheet is overlaid on the ink-repellant layer. Optionally, an adhesive layer may be present between the coating and the sheet. Said cover sheet enables the loosely bound debris which is produced in the image areas on exposure to be trapped and, thus, be  
15 prevented from being released to the atmosphere. The debris may then be removed from the exposed precursor simply by removal of the sheet prior to inking. The sheet may be comprised of, for example, polypropylene or poly(ethylene terephthalate), or other suitable film  
20 material which is transparent to infra-red radiation. Thus, for example, the cover sheet may be formed from a masking film having a structure and composition as described in EP-A-323880. The thickness of the sheet may be within the range of from 8 $\mu$ m to 100 $\mu$ m.

25 The driographic plate precursor may also contain an anti-reflective layer coated on the cover sheet. Suitable anti-reflective coatings are described in US Patent Nos. 3,793,022 and 4,769,306 and have a refractive index of from 1.0 to 1.6, preferably about  
30 1.3. Suitable materials for inclusion in the anti-reflective layer include, for example, fluorinated polymers available from Du Pont under the trade name Zonyl®.

In use, the driographic plate precursor is imaged  
35 by a beam of radiation from a laser operating in the infra-red region of the spectrum. Particularly

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preferred are YAG lasers and diode lasers, for example the Sanyo SDL-7032-101 100 mW diode laser, set to deliver energy of up to  $3000 \text{ mJ/cm}^2$  to the coating. Exposure to the beam of radiation causes ablation of the coating, which in turn drives away the repellant material. Loosely bound debris on the exposed precursor may then simply be peeled away together with the cover sheet to reveal the underlying ink-receptive surface. The remaining, unimaged, areas do not accept ink. The images produced show a high degree of resolution.

The following Examples are illustrative of the invention:

Example 1

This example demonstrates that the precursor of the present invention can be exposed with an infra-red diode laser to impart an image which accepts drierographic printing ink.

An infra-red absorbing ablatable composition was prepared by mixing the following ingredients:

Ciba-Geigy Microlith® CWA	30.0 g
Ethanol, 95% in water	18.0 g
Distilled water	50.0 g
Ammonia	2.0 g

to form a uniform mixture. (The binder of the Microlith CWA constituted the ablatable polymer). The viscosity of the mixture was reduced by adding 100.0 g of distilled water, and the mixture was coated onto Howcolon® polyester film with a wire-wound bar. The coating was dried in an oven for 90 seconds at  $100^\circ\text{C}$ . The coating weight after drying was  $1.02 \text{ g/m}^2$ . Both the coating and the substrate accepted drierographic ink.

A silicone coating composition was prepared by mixing the following ingredients:

Dow-Corning Syl-Off® 7046	5.7 g
Isopar® H	59.3 g

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Dow-Corning Syl-Off® 7048

0.1 g

to form a uniform mixture (Isopar H is a proprietary hydrocarbon liquid). The silicone mixture was spin-coated at 100 RPM onto the ablatable layer, forming a  
5 silicone overcoat with a coating weight of  $0.78 \text{ g/m}^2$ . The overcoat was cured at  $140^\circ\text{C}$  for 5 minutes. The overcoated film repelled drierographic ink.

The resultant precursor was mounted on a motor-driven drum and imaged on the coated side with a  
10 scanning diode laser (Sharp LT015MDO, 40mW, 828 nm) configured to deliver 30 mW continuous wave to a 15 micron spot.

A plurality of precursors was imaged in this way using different energies. This was effected by  
15 changing the rotation speed of the drum which alters the exposure time per spot i.e. the so-called "dwell-time". The dwell time was varied from 10µsec ( $200 \text{ mJ/cm}^2$ ) to 30µsec ( $600 \text{ mJ/cm}^2$ ).

Upon exposure to the infra-red radiation, the  
20 ablatable layer ablated from the substrate in the image areas thereby removing the overlying silicone layer in those areas to reveal the underlying ink-accepting material. The surface of each exposed precursor was rubbed lightly with Isopar® H-dipped cotton cloth to  
25 removed loose debris and was then allowed to dry. The dried precursors were then inked with DaiNippon Dricolor® QS magenta ink using a roller applicator. The images which had been produced with greater than about  $500 \text{ mJ/cm}^2$  accepted ink, whereas the areas which  
30 were unexposed, or which were exposed with less than about  $500 \text{ mJ/cm}^2$ , remained clean.

#### Example 2

This example demonstrates that the thickness of the ink-repellant overlayer can be varied by a factor  
35 of three without affecting sensitivity or resolution.

An infra-red absorbing ablatable composition was

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prepared and coated onto Howcolon® polyester substrate as described in Example 1. The coating weight after drying was  $3.1 \text{ g/m}^2$ . Both the coating and the substrate accepted driographic ink.

- 5 A silicone coating composition was prepared by mixing the following ingredients:

Dow-Corning Syl-Off® 7046	20.0 g
Isopar® H	119.8 g
Dow-Corning Syl-Off® 7048	0.2 g

- 10 to form a uniform mixture. The silicone mixture was spin-coated at 100 RPM onto the ablatable coating to form a silicone overcoat with a coating weight of  $2.1 \text{ g/m}^2$ . The experiment was repeated with the silicone bath diluted 1:1 with an equal weight of Isopar® H to  
15 form a silicone overcoat with a coating weight of  $0.73 \text{ g/m}^2$ . In each case, the overcoat was cured at  $140^\circ\text{C}$  for 5 minutes and repelled driographic ink.

- A plurality of the resultant precursors were mounted on a motor-driven drum and imaged on the coated  
20 side with a scanning diode laser (Sanyo SDL-7032-101, 100 mW, 8302 nm) configured to deliver 55 mW continuous wave to a 25 micron spot. The energies delivered to the precursors were varied by changing the rotation speed of the drum, which altered the dwell time. The  
25 dwell times varied from  $23 \mu\text{sec}$  ( $400 \text{ mJ/cm}^2$ ) to  $124 \mu\text{sec}$  ( $2300 \text{ mJ/cm}^2$ ).

- Upon exposure, the infra-red absorbing layer ablated from the substrate, removing the overlying silicone layer and revealing ink-accepting material.  
30 The total amount of silicone and ablatable polymer debris which remained in the exposed areas in each case was estimated by examining the coatings at 100 times magnification and is given in the table below.

- To remove debris, the exposed precursors were  
35 rubbed lightly with Isopar® H-dipped cotton cloth and allowed to dry. The resultant printing plates were

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then inked with DaiNippon Dricolor magenta ink using a roller applicator. The imaged areas accepted ink with no discernible difference between the two layers of different coating weight. Inked resolution was

- 5 estimated by examining the plates at 100 times magnification. As the table shows, features imaged at the shortest dwell times had resolution narrower than 10 microns while at the longest dwell time, the feature size increased to about 20 microns.

	Dwell Time ( $\mu$ sec)	Energy (mJ/cm <sup>2</sup> )	Feature Size ( $\mu$ m)	Percentage Remaining Debris 3.1 g/m <sup>2</sup> Ablatable Layer	
				0.73 g/m <sup>2</sup> Silicone	2.1 g/m <sup>2</sup> Silicone
	207	2320	20	10	10
15	127	1428	20	20	20
	93	1040	15	20	20
	72	803	15	30	50
	63	702	15	30	60
	53	596	12	30	50
20	46	519	10	40	50
	42	465	10	40	50
	40	449	9	50	50
	38	422	8	50	50

### Example 3

This example demonstrates a composition which ablates from a conventional aluminium printing plate substrate when exposed with an infra-red diode laser.

- 30 Infra-red absorbing ablatable compositions were prepared by mixing the following ingredients:

#### A. 10% Sensitiser

	Polymethylmethacrylate	
	(Medium Molecular Weight, Aldrich)	10.8 g
35	Ciba-Geigy Microlith® CA	1.2 g
	Methyl Ethyl Ketone (MEK)	178.0 g
	Dow-Corning 1248 wetting agent	3.0 ml

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## B. 18% Sensitiser

	Polymethylmethacrylate	
	(Medium Molecular Weight, Aldrich)	10.8 g
	Ciba-Geigy Microlith® CA	2.4 g
5	Methyl Ethyl Ketone (MEK)	178.0 g
	Dow-Corning 1248 wetting agent	3.0 ml

to form uniform mixtures. The mixtures were coated onto 30 gauge anodised aluminum sheets by whirling at 100 RPM, and the coatings were then dried at 60°C for 30 seconds. Each mixture was then diluted by adding MEK in an amount equal to the mass of the mixture and the experiment was repeated to obtain coated sheets of reduced coating weight. Each mixture was then diluted once more with an equal mass of MEK, and used to obtain further coated sheets of even further reduced coating weight. The coated sheets were mounted on a motor-driven drum and imaged on the coated side with a scanning diode laser (Sharp LTO15MD, 40 mW, 828 nm) configured to deliver 30 mW continuous wave to a 15 micron spot. The dwell times were varied from 10µsec (200 mJ/cm<sup>2</sup>) to 30µsec (600 mJ/cm<sup>2</sup>) by changing the rotation rate of the drum. In certain cases i.e. where low energy exposures or low sensitivity levels, or a combination of both variants, were employed, ablation was incomplete, and a roughened surface was observed when the coating was examined under magnification. When higher energy exposures or higher sensitivity levels, or a combination of both variants, were employed, the coating ablated completely and ablated line widths could be determined. Typical results are summarised in the following table:

	Coating Weight (g/m <sup>2</sup> )	Sensitiser Percentage	Width of Ablated Line (μm)	
			200 mJ/cm <sup>2</sup>	600 mJ/cm <sup>2</sup>
5	0.4	18	5	10
	1.0	18	(incomplete ablation)	5
	2.1	18	(incomplete ablation)	5
	0.4	10	(incomplete ablation)	14
	1.1	10	(incomplete ablation)	7
	2.6	10	(incomplete ablation)	5
10				

### Example 4

This example demonstrates that metallised polyester coated sequentially with a primer layer, an  
15 ablatable layer, and an ink-repellant overlayer can be imaged by infra-red diode laser and inked with driographic ink to form a high resolution image.

A primer layer was prepared by mixing the following ingredients:

20	Epikote® 1004	5g
	Methyl Ethyl Ketone	100 ml

The primer layer was coated onto Mylar® pre-coated with a 50 nm thick layer of smooth aluminum using a wire-wound bar and oven dried at 140°C for 30 seconds, reaching a dry coating weight of 2.69 g/m<sup>2</sup>.

An infra-red absorbing ablatable composition was prepared by mixing the following ingredients:

	Polymethylmethacrylate	
	(Low Molecular Weight, Aldrich)	20 g
30	Microlith® Black CK	5 g
	Methyl Ethyl Ketone	100 ml

This mixture was coated using a wire-wound bar onto the primer layer and oven dried at 140°C for 30 seconds, reaching a dry coating weight of 3.17 g/m<sup>2</sup>.

35       An ink-repellant layer was prepared by mixing the  
following ingredients:

Dow-Corning Syl-Off® 7046	20.0 g
Isopar® H	40.0 g

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Dow-Corning Syl-Off® 7048 0.5 g

Dow-Corning Syl-Off® 297 0.2 g

until a uniform mixture was achieved. The mixture was coated onto the primed ablatable layer with a wire-wound bar and then oven cured at 140°C for 2 minutes. The dry coating weight of the ink-repellant layer was 0.83 g/m<sup>2</sup>. The coating rejected drierographic ink.

The resultant precursor was exposed with an infra-red laser according to Example 1. On exposure at 600 mJ/cm<sup>2</sup>, the coating ablated. When viewed at 100 times magnification, the ablated areas could be seen as clearly defined lines, less than 10µm wide. The plate was wiped with an Isopar® H-dipped cloth and allowed to dry at room temperature. When drierographic ink was applied according to Example 1, the image areas accepted ink, while the unexposed areas rejected it.

#### Example 5

This example demonstrates the use of an ablatable layer with improved sensitivity, together with a drierographic overlayer.

An infra-red absorbing ablatable composition was prepared comprising the following composition:

Microlith® Black CK 5g

Methyl Ethyl Ketone 100 ml

The mixture was coated using a wire wound bar onto aluminium coated Mylar® as used in Example 4. The coated film was oven dried at 140°C for 30 seconds. The coating weight was 0.17 g/m<sup>2</sup>.

The coated film was then overcoated with an ink-repellant layer according to Example 4, and the resultant precursor exposed to an infra-red laser according to Example 1. On exposure at 200 mJ/cm<sup>2</sup>, the infra-red absorbing layer ablated, removing the ink-repellant overcoat. When viewed with a microscope the ablated areas could be seen as clearly defined lines, less than 10µm wide.

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When driographic ink was applied according to Example 1, the ablated areas accepted ink whereas the unexposed areas reject it.

Example 6

- 5 An infra-red absorbing ablatable composition was prepared by blending the following ingredients:

Dispercel® CBJ-A	2.0 g
MEK	8.0 g

- to form a uniform mixture. The mixture was coated on  
10 Howcolon® polyester using a No. 5 gauge wire-wound bar and allowed to air dry for five minutes to form a coating with a dry weight of around 1.0 g/m<sup>2</sup>.

A silicone coating composition was prepared by mixing the following ingredients:

- |    |                           |        |
|----|---------------------------|--------|
| 15 | Dow-Corning Syl-Off® 7046 | 20.0 g |
|    | Dow-Corning Syl-Off® 7048 | 0.05 g |
|    | Dow-Corning Syl-Off® 297  | 0.5 g  |
|    | Dow-Corning Syl-Off® 7210 | 5.0 g  |
|    | Isopar® G                 | 40.5 g |

- 20 to form a uniform mixture (Isopar G is a proprietary liquid hydrocarbon). The silicone mixture was coated onto the ablatable layer using a No. 8 gauge wire-wound bar and cured at 130°C for 3 minutes. The resultant precursor was cut into two pieces and mounted on the  
25 motor-driven drum of the write engine described in Example 3. Onto one of the precursors, there was applied a cover sheet in the form of a clear adhesive overlay film. Onto the other precursor there was taped an 8µm Mylar® cover sheet bearing no adhesive. The  
30 precursors were then exposed as described in Example 3. When the adhesive cover sheet was removed, it bore the image written by the laser, consisting of ablated pigment, polymer residue, and silicone ablated from the film. The non-adhesive cover sheet bore a much fainter  
35 image. Without wiping away loose debris, the two exposed precursors were inked as described earlier, and

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the inked images were contact-transferred to smooth paper. The precursor which had been provided with the adhesive cover sheet printed a clear image, whereas the precursors which had been provided with the non-  
5 adhesive cover sheet printed a faint, patchy image. Thus, the adhesive cover sheet was an excellent means for not only trapping ablated material, but also for removing loose debris thus obviating the need for a cleaning step. The adhesive cover sheet also carried a  
10 copy of the printed image, allowing verification of the exposure.

Example 7

This example demonstrates that driographic plate precursors of the present invention can be imaged by  
15 continuous-wave infra-red diodes in a computer-driven write engine.

An infra-red absorbing ablatable composition was prepared by blending the following ingredients:

20	Dispercel® CBJ-A	2.0 g
	MEK	8.0 g

to form a uniform mixture. This mixture was coated on Howcolon® polyester using a No. 5 gauge wire-wound bar and allowed to air dry for five minutes to form a coating with a dry weight of around 1.0 g/m<sup>2</sup>.

25 A silicone coating composition was prepared by mixing the following ingredients:

	Syl-Off® 7046	20.0 g
	Syl-Off® 7048	0.5 g
	Syl-Off® 297	0.2 g
30	Isopar® G	40.0 g

to form a uniform mixture. The silicone mixture was coated onto the ablatable layer using a No. 8 gauge wire-wound bar and cured at 130°C for 3 minutes. A Mylar cover sheet was then applied. The resultant  
35 precursor was exposed through the cover sheet on a write engine supplied by CREO (Vancouver BC) using an

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array of 32 infra-red lasers emitting at 830 nm (Sanyo Semiconductor, SDL-7032-102, Allendale, NJ), to produce a 150 line screen text pattern, using  $130 \text{ mJ/cm}^2$  of incident laser energy. The imaged precursor was removed from the drum and loose debris was wiped away with an Isopar® H-dampened cloth. The resultant printing plate was inked as described previously, and the inked image was contact-transferred to smooth paper. A recognisable image was printed.

10        Example 8

Example 6 was repeated using Automask® material as the adhesive overlay film. Automask® is a laminated sheet product supplied by Autotype International Ltd for use as a masking film in the preparation of lithographic plates and screen printing stencils.

The red adhesive coated membrane was separated from the base film and applied to the surface of the ink repellant layer. The precursor was exposed as described in Example 3 and the membrane was removed. The resultant plate was found to be free of loose debris and did not require a cleaning step prior to printing.

The adhesive of the membrane was based on a natural rubber, with the addition of an alpha terpene resin to improve tack, and provided a peel resistance of 37-70 gm/30 mm sample width measured at an angle of  $180^\circ$  when the membrane and the base film were separated.

30        Example 9

Example 6 was repeated using a cover sheet provided in situ. An adhesive sublayer was produced by applying a solution of natural rubber (12g) and an alpha terpene resin (100 g) in hydrocarbon solvent (5000 ml) to the surface of the silicone layer of the ablatable precursor assembly described in Example 6.

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When dry, a composition comprising a solution of an aliphatic polyurethane resin and cellulose nitrate as described in Example 1B of European Patent No.323,880 was coated over the adhesive layer to a thickness of 30  
5 microns.

The precursor was exposed as described in Example 3. The cover sheet was removed to obtain a printing plate requiring no cleaning stage prior to printing.

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CLAIMS:

1. A driographic plate precursor comprising a  
base substrate carrying an infra-red radiation  
ablatable ink repellent coating, the coating being  
5 covered with a transparent cover sheet.
2. A plate precursor as claimed in claim 1  
wherein the coating is in the form of a single layer  
comprising an infra-red radiation ablatable material  
and an ink repellent material.
- 10 3. A plate precursor as claimed in claim 1  
wherein the coating includes a layer comprising an  
infra-red radiation ablatable material and an outer  
layer comprising an ink repellent material.
4. A plate precursor as claimed in claim 2 or 3  
15 wherein the infra-red radiation ablatable material  
comprises an ablatable polymer and an infra-red  
radiation absorber.
5. A plate precursor as claimed in claim 4  
wherein the ablatable polymer is an acrylic polymer or  
20 a self-oxidising polymer.
6. A plate precursor as claimed in claim 4 or 5  
wherein the infra-red radiation absorber is carbon  
black or an infra-red sensitising dye.
7. A plate precursor as claimed in any one of  
25 claims 2 to 6 wherein the ink repellent material is a  
silicone polymer.
8. A plate precursor as claimed in any preceding  
claim wherein the cover sheet is adhered to the  
coating.
- 30 9. A method of image formation which comprises  
(a) providing a driographic plate precursor  
comprising:  
a base substrate carrying an infra-red  
radiation ablatable ink repellent coating  
35 covered with a transparent cover sheet,  
(b) image-wise exposing the precursor by

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directing the beam from an infra-red laser at sequential areas of the coating so that the coating ablates and loses its ink repellancy in those areas to form an image,

5 (c) removing the cover sheet and ablation products, and

(d) inking the image.

10. A method according to claim 9 wherein an anti-reflective layer is provided on the cover sheet.

10

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 93/01413

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 B41C1/055; B41N1/14		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	B41C ; B41N ; B41M	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	GB,A,2 021 276 (POLYCHROME CORPORATION) 28 November 1979 see page 1, line 1 - line 42; figure 2 see page 2, line 62 - line 70 see page 5, line 102 - line 108 ---	1-10
X	US,A,3 962 513 (A.C.EAMES) 8 June 1976 see column 2, line 33 - line 68; figures 1,2 ---	1-10
X	GB,A,1 448 838 (KANSAI PAINT COMPANY) 8 September 1976 see page 1, line 56 - page 2, line 78 see page 3, line 47 - page 4, line 33 ---	1-10
-/--		
<sup>10</sup> Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search 02 SEPTEMBER 1993		Date of Mailing of this International Search Report 17 09. 93
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer BACON A.J. <i>A. J. Bacon</i>

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	EP,A,0 160 395 (IMPERIAL CHEMICAL INDUSTRIES PLC) 6 November 1985 see page 4, line 1 - line 8 see page 7, line 1 - line 13 see page 8, line 7 - line 17 -----	1-10

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9301413  
SA 76244

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

02/09/93

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US-A-3962513	08-06-76	None	
GB-A-1448838	08-09-76	JP-A- 49118501 JP-C- 998265 JP-A- 49072003 JP-B- 54031401	13-11-74 30-05-80 11-07-74 06-10-79
EP-A-0160395	06-11-85	DE-A- 3584989	06-02-92

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